



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number: 0 589 681 A2

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 93307478.3

(51) Int. Cl.<sup>5</sup>: C09C 1/24

(22) Date of filing: 22.09.93

(30) Priority: 22.09.92 JP 277897/92

(43) Date of publication of application:  
30.03.94 Bulletin 94/13

(84) Designated Contracting States:  
DE FR GB IT NL

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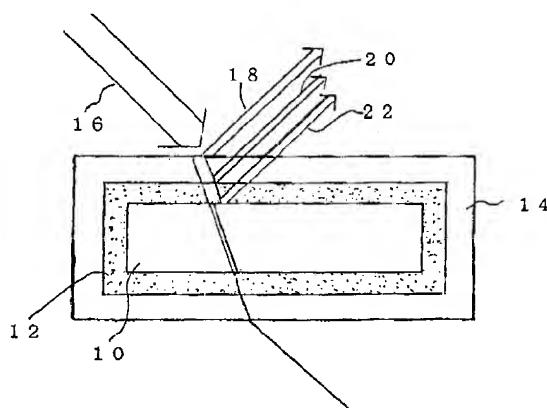
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### (54) Red pigment and manufacturing method for it.

(57) A red pigment comprising: a plate type particle (10), such as mica, coated with an iron oxide (12), and an aluminum compound layer (14) which contains at least aluminum oxide and which is formed on the iron oxide. The optical thickness of the aluminum compound layer (14) is 150-500 nm.

The red pigment according to the present invention has excellent color tone with high chroma from the orange to the blue red and, moreover, has excellent stability.



F I G. 1

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This invention relates to a red pigment and manufacturing method thereof, and more particularly to an improvement of red pigment and manufacturing method thereof comprised of inorganic materials.

A red pigment is used in various fields such as the cosmetics, a paint for automobile, a general paint, a plastic, an ink, a synthetic leather, a print, sundries, a furniture, an ornament, a fabric and a general sundries.

As a conventional red pigment, there are many pigments containing a red organic substance such as a carmine. However, the conventional red pigment had a various demerits such as discoloring of these organic substance, and unsafety for human body.

On the other hand, a red pigment containing a red iron oxide as an inorganic red pigment is well-known.

Namely, as examples of the red pigment which are composed of inorganic substances, lamella mica particle of which a surface is coated with the red iron oxide, a titanium dioxide coated mica particle on which the iron oxide is further coated, and plate type red iron oxide itself are cited.

The inorganic red pigment composed of a red iron oxide has various merit such as excellent safety and sunproof.

However, the red pigment composed of the above red iron oxide is limited the red color thereof to brown red which is the color of the iron oxide itself. Also, the conventional inorganic red pigment could not present the appearance color as a hue of various red color like the organic pigment.

It is possible to change the color tone of pigment into e.g. coating the surface of mica particle with the red iron oxide and an inorganic substances which has other color tone. However, in this case, the mixture of the material of more than one substances must be coated on the surface of the mica particle. However, this coating treatment is difficult and the mixture of the substances causes a problem to make the hue to gradually be black because each material absorbs light and the lightness of the pigment declines notably.

Accordingly, it is an object of the present invention to eliminate the problems of the prior art and provide a red pigment which comprised of inorganic substances which presents high lightness and has the color tone of vivid red and a manufacturing method thereof.

As a result of studies undertaken by the present inventors so as to achieve this aim, it has been found that it is possible to obtain the red pigment by forming a red iron oxide like plate and coating the plate type red iron oxide with an aluminum compound. On the basis of this finding, the present invention has been achieved.

Accordingly, in the first aspect of the present invention, there is provided a red pigment comprising;

an iron oxide plate type particle,  
an aluminum compound layer which contains at least aluminum oxide and which is formed on the iron oxide plate type particle,  
and the optical thickness of the aluminum compound layer being 150-500 nm.

In the second aspect of the present invention, there is provided a red pigment according to claim 1 further comprising;

an iron oxide layer which is formed on the plate type particle,  
optical thickness of the iron oxide layer being 60-350 nm,  
and optical thickness of the aluminum compound layer being 150-500 nm.

In the third aspect of the present invention, there is provided a red pigment according to claim 1, wherein said aluminum compound layer contains 1-20 weight % of iron oxide and / or compound of iron oxide-alumina.

In the fourth aspect of the present invention, there is provided a manufacturing method of a red pigment according to claim 3 comprising;

forming an iron oxide coated plate type particle of which the content of the coated iron oxide is from 20 to 100 weight % for the plate type particle by coating the plate type particle using a coating bath containing a precursor of the iron oxide according to a precipitator method,

forming an aluminum compound coated iron oxide coated plate type particle of which content of the aluminum compound is from 15 to 60 weight % for the iron oxide coated plate type particle by coating the iron oxide coated plate type particle using a coating bath containing a precursor of the aluminum compound according to a precipitator method,

and heating the aluminum compound coated iron oxide coated plate type particle at 100 - 900 °C.

In the fifth aspect of the present invention, there is provided a manufacturing method according to claim 4 characterized in that a precursor of iron oxide is added to the coating bath of aluminum compound so as to be 1 to 20 weight % of iron oxide and / or iron oxide-aluminum compound for the iron oxide coated plate type particle.

The composition of this invention are explained in detail hereinafter.

The plate type iron oxide in the invention can be obtained to form the iron oxide itself like a plate. However, it is preferable to coat a plate particle by the iron oxide. As examples of the plate particles, muscovite mica, biotite, gold mica, synthetic mica, red mica, lithia mica, talc, kaolin, sericite, plate type silica, plate type alumina,

plate type titanium dioxide, plate type iron oxide, mica titanium aluminum flake powder, and stainless powder. Also, it is possible to use the commercially available iron oxide coated mica as the intermediate of the red pigment of the invention.

Also, the particle diameter of the plate type particles are not especially limited. However, the red pigment of the invention is preferably used as the pigment of the general industrial products such as the cosmetics. In this case, as for the plate type particle, it is preferable to use the particles of which the particle diameter is about 1-50 µm and the shape is as flat as possible to obtain a beautiful red color.

For examples of the iron oxide which is used to coat the plate type particle as an intermediate when manufacturing the red pigment of the invention, iron oxide of which the color thereof is from the red to brown and  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}$  can be cited. The plate type particle is coated with the single kind of the iron oxide or equal to or more than two kinds of mixtures thereof.

Also, iron oxide hydrate  $\text{FeO(OH)}$  or black iron oxide ( $\text{Fe}_3\text{O}_4$ ) which will be oxidized to  $\text{Fe}_2\text{O}_3$  at the heating process can be used.

The optical thickness of the iron oxide layer is preferably 60 - 350 nm. In case of the diameter of plate type particle being 1 - 50 µm, the content of the iron oxide is 20-100 weight % for the plate type particle 100 weight % and preferably 30-80 weight %.

If the content of the coating iron oxide is less than 20 weight %, the red color tone tends to become weak. If the content of the iron oxide is over 100 weight %, the color tone of the iron oxide is too emphasized and it is not preferable for the color tone being brown which is the color tone of the iron oxide itself.

The optical thickness of the layer means the thickness to multiply an index of refraction by geometrical thickness of the layer.

On the other hand, the aluminum compound which is used in the invention contains aluminum oxide  $\text{Al}_2\text{O}_3$  as an essential ingredient. Besides, aluminum oxide hydrate  $\text{Al}_2\text{O}_3(\text{H}_2\text{O})$ ,  $\text{Al}_2\text{O}_3(3\text{H}_2\text{O})$  and aluminum hydroxide and so on may be mixed.

The optical thickness of the aluminum compound layer is preferably 150-500 nm. In case of the diameter of the plate type particle being 1-50 µm. the aluminum compound content is 15-60 weight % for 100 weight % of the iron oxide coated plate type particle as the intermediate and preferably 20-40 weight %.

In case of content of the aluminum compound being less than 15 weight % for 100 weight % of the iron oxide coated plate type particle, it isn't possible to adjust the color tone of the original iron oxide. Also, if the content of the aluminum compound is over 60 weight %, the notable decline of chroma may be happened.

In case of content of the aluminum compound being equal to or less than 25 weight % for 100 weight % of the plate type particle which is coated with the iron oxide as an intermediate, orange color tone is obtained. In case of the content of the aluminum compound being 25-40 weight %, blue red color tone is obtained. In case of content of aluminum compound being equal to or more than 40 weight %, yellow red color tone is obtained.

In the coating process of the aluminum compound to iron oxide coated plate type particle as the intermediate of the invention, the heating temperature is 100-900°C and preferably 300-800°C. If the heating temperature exceeds 900°C, the particle agglutination may happens.

Moreover, if iron oxide and / or compound of iron oxide-alumina are mixed in the aluminum compound, it is possible to further improve the chroma of the red pigment. The content of the iron oxide and / or iron oxide-oxide of alumina compound is 1 to 20 weight % and preferably 5 to 15 weight %.

As the manufacturing method of the red pigment according to the invention, it is possible to cite the following method.

Namely, as examples of the method,  
 (1) dispersing the commercially available particle of the muscovite pigment in water, gradually adding an aqueous solution of iron salt such as iron chloride (I), iron chloride (II), iron sulfate (I), iron sulfate (II), iron nitrate (I) and iron nitrate (II) and an alkaline aqueous solution such as a solution of sodium hydroxide, potassium hydroxide into the dispersed water keeping the pH being constant, coating hydrated iron oxide on the surface of the plate type particle by the neutralization decomposition, and heating at the 300-800°C,

(2) dispersing the commercially available particle of the muscovite pigment in water, adding an aqueous solution of iron salt such as iron chloride (I), iron chloride (II), iron sulfate (I), iron sulfate (II), iron nitrate (I), iron nitrate (II), and urea, heating at 80 - 100 °C for neutralization , coating the plate type particle with iron oxide hydrate and heating at the 150-800 °C,

(3) vaporizing the iron compound at high temperature and coating the iron oxide on the plate type particle directly.

Also, as methods of coating the iron oxide coated intermediate of the invention with the aluminum compound, the following methods are cited.

(1) dispersing the iron oxide coated plate type particle in water, adding gradually a water solution of alu-

5 minum salt such as aluminum chloride, aluminum sulfate and aluminum nitrate and alkaline solution such as a solution of sodium hydroxide, potassium hydroxide keeping a pH of the system being constant, coating hydrated aluminum oxide by the neutralization decomposition and heating at the 150-700 °C,

(2) dispersing the iron oxide coated plate type particle in water, adding an aqueous solution of iron salt such as aluminum chloride, aluminum sulfate, aluminum nitrate and urea, heating at 80 - 100 °C for neutralization decomposition, coating the plate type particle with hydrated aluminum oxide and heating at the 150-800°C.

10 Also, as an example of mixing iron oxide and / or compound of iron oxide- alumina into the aluminum compound, at the coating the iron oxide coated plate type particle with the aluminum compound which contains aluminum oxide, water solution of the iron salt is mixed in the water solution of aluminum salt and coating by the neutralization decomposition described above.

15 The red pigment according to the invention as above-mentioned is using the aluminum compound for adjusting the color tone which the red iron oxide has. Namely, generally speaking, prior pigment contains substances which absorbs light component having a certain wavelength and reflects light component having the other wavelength. Accordingly, if the prior pigment is irradiated by white light which is the aggregate of the light component having various wavelength, the light component with the specified wavelength in the white light is absorbed by the pigment. Therefore, the color tone of the above pigment is determined by the reflected light which is the complementary color to the absorption light.

20 Namely, in the case of the red iron oxide, the brown red color which is the color of the iron oxide corresponds to the reflected light.

And then, in the point of view of general pigment, it is necessary to add a substance which absorbs light giving the other wavelength to the pigment for adjusting the color of pigment.

However, in this case, an absorption wavelength area is magnified. The color tone of the pigment gradually changes to achrocoatic color and the chroma has declined.

25 Therefore, the inventors used the interference operation of the light and adjusted the color tone of the iron oxide.

Namely, the surface of the plate type particle is coated with the iron oxide and this iron oxide coated particle is coated with the aluminum compound. In this case, pigment structure is described as shown in the figure 1.

30 In the figure, the shape of the mica 10 is plate like, and the iron oxide 12 is coated on the plate type mica 10. And then, the layer 14 of the aluminum compound which contains aluminum oxide is coated around the iron oxide layer 12. The aluminum compound 14 and the mica 10 is white and the transmittance of the light is high. Also, the iron oxide layer 12 has brown red color as described above.

If the white light 16 is irradiated to the pigment, a part of this irradiation light 16 becomes the white reflected light 18 which was reflected on the surface of the aluminum compound layer 14. Also, a part of light having a certain wavelength area is absorbed by the iron oxide and the reflected lights 20, 22 which were reflected on the surface of the mica 10 and the surface of the iron oxide layer 12, respectively and the reflected lights 20, 22 become the brown red light.

40 And then, the white reflected light 18 and the red reflected lights 20, 22 causes interference, and the light component having the specific wavelength of the red reflected lights 20, 22 is emphasized. Therefore, a reflected light (the interference light) with sharp color tone can be obtained.

Namely, as is clear form the figure 2, the white reflected light 18 and the red reflected lights 20, 22 have the optical path difference which depends on the layer thickness of the aluminum compound layer 14. And then, in the reflected lights 20, 22, the light component having wavelength as shown in figure 2(A) and the light component having the same wavelength in reflected light 18 have a optical path difference (L:about twice of the aluminum compound layer). Accordingly, a part of peak of the light component of the red reflected lights 20, 22 is situated on a part of trough of the light component of white light 18. As a result, both light components deny each other and it has disappeared as shown in the figure (C).

50 However, as shown in the figure (D), in case of the light component having half wavelength comparing the figure (A), the light component of white reflected light 18 and the red reflected lights 20, 22 are shifted from each other for 1 wavelength. Therefore, the part of peak of both and the part of trough is overlapped and amplitude of vibration amplification is done as shown in the figure (F).

As a result, only the light with the specific wavelength of red reflected lights 20, 22 is emphasized and can obtain a color tone more distantly sharp than the reflected light of iron oxide itself.

55 As described above, the aluminum compound is coated by the red pigment in the invention. However, the light transmittance of the aluminum compound is very high. Therefore, the total quantity of light of reflected lights 18, 20, 22 scarcely declines comparing the case using the pigment mixed more than one substances, the chroma never declines notably.

In case of this invention, color tone is adjusted by the interference operation.

Therefore, the optical path difference generates the interference operation and becomes important material of this invention. As is clear from the figure 2, when the optical path difference becomes a half wavelength of the wavelength of the light component, the light strength of this wavelength area decreases. On the other hand, the optical path difference becomes same or integer magnification length of the wavelength of the light component, the light strength of this wavelength area increases. Therefore, it is necessary to adjust the path length to adjust the strength of the visible light area by the optical path difference.

Also, in the example which is shown in the figure 1, reflected light 18 was a white light. However, if the aluminum compound contains iron oxide and / or iron oxide-oxide of alumina compound, reflected light 18 becomes red light. As a result, it is possible to adjust tone of color with the interference operation of the red reflected lights 18, 20, 22. As a result, it becomes possible to especially improve the chroma.

As mentioned above, the red pigment of the invention uses the interference of the light which depended on the layer thickness of the aluminum compound layer 14. As a result, the tone color, lightness and the chroma of the red pigment is excellently improved.

Moreover, the red pigment is manufactured from the inorganic substances which contains the iron oxide and the aluminum compound. Therefore, it is very excellent about stability, safety, sunproof, acid resistance, alkali resistance, solvent resistance, the heat resisting property and so on.

#### [BRIEF DESCRIPTION OF THE DRAWINGS]

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Figure 1 and figure 2 are the explanation views which show the color tone adjustment operation of the red pigment according to the present invention.

#### [EXAMPLES]

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Preferred embodiment of the present invention will be explained hereinunder. The content is expressed by weight %.

#### RELATION OF COLOR TONE AND LAYER THICKNESS

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Relation between thickness of the aluminum compound layer and the color tone is explained hereinafter.

Red pigments having various layer thickness of the aluminum compound is produced by the following method and examined the color tone thereof.

35

100 g of commercially available muscovite (the average particle size ; 30  $\mu\text{m}$ ) is dispersed in 500 ml of water. 10 wt % of ferric chloride (6 hydrate) is added at the 5 ml / min. under heating the system at 90 °C and stirring condition. 0.5 N sodium hydroxide solution is added to maintain the pH of the system to 4.5-5.0 until ending the reaction. The product is filtrated and dried and heated at 500°C for 2 hours. As a result, iron oxide coated mica is obtained.

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100 g of the iron oxide coated mica, aluminum sulfate (14 hydrate) and 200 g of urea is dispersed in 1000 ml of water, heated and stirred it for 4 hours in boiling condition. After washing by water, filtering and drying, the aluminum oxide coated iron oxide coated mica is obtained by heating at 500°C in the atmosphere.

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The color tone was examined by the following method. Namely, 5 g of the red pigments is filled to the quartz cell which is for measurement of color tone of powder. After orientation of the pigments, the pigments are pressed at the constant pressure and samples for the measurement are obtained. Next, the samples are measured with the spectrum colorimetry measuring apparatus (HITACHI C-2000).

Also, thickness of the layer is indicated by the optical thickness of the layer.

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Table - 1

Ferric chloride content; 33.75 g		Thickness of iron oxide layer;30 nm						
		0	31	95	160	220	315	380
5	Aluminum sulfate content (g)	0	50	150	250	350	500	600
	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
10	H.V./C	3.0R 3.8 /6.80	3.8R 4.3 /6.81	4.8R 4.98 /7.06	3.9R 5.16 /7.06	4.0R 5.18 /7.26	4.5R 5.0 /7.40	3.0R 4.44 /1.00

Table - 2

Ferric chloride content; 45.0 g		Thickness of iron oxide layer;60 nm						
		0	31	95	160	220	315	380
15	Aluminum sulfate content (g)	0	50	150	250	350	500	600
	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
20	H.V./C	3.5R 3.34 /6.92	3.7R 3.60 /6.95	8.4R 4.42 /7.78	2.3R 4.81 /8.31	7.4R 4.80 /8.16	7.0R 4.69 /7.54	5.3R 4.00 /6.06
25								

Table - 3

Ferric chloride content; 120.0 g		Thickness of iron oxide layer;70 nm						
		0	31	95	160	220	315	380
30	Aluminum sulfate content (g)	0	50	150	250	350	500	600
	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
35	H.V./C	3.5R 3.19 /6.90	3.7R 3.30 /6.90	8.5R 4.08 /7.88	0.3R 4.80 /8.48	6.4R 4.90 /8.22	5.7R 4.42 /7.50	3.5R 3.48 /6.10

Table - 4

Ferric chloride content; 200.0 g		Thickness of iron oxide layer;250 nm						
		0	31	95	160	220	315	380
45	Aluminum sulfate content (g)	0	50	150	250	350	500	600
	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
50	H.V./C	3.5R 3.00 /7.00	3.7R 3.12 /7.05	7.1R 4.01 /8.10	9.3RP 4.44 /8.52	6.1R 4.81 /8.33	5.3R 4.01 /8.14	3.0R 3.08 /6.22

Table - 5

Ferric chloride content; 260.0 g		Thickness of iron oxide layer;350 nm						
5	Aluminum sulfate content (g)	0	31	95	160	220	315	380
	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
	H.V./C	3.5R	3.8R	8.0R	0.8R	6.8R	6.0R	4.0R
10		2.80	2.84	3.23	4.12	4.36	3.43	2.80
		/6.85	/6.86	/7.60	/8.28	/8.16	/7.40	/6.18

Table - 6

Ferric chloride content; 350.0 g		Thickness of iron oxide layer;450 nm						
15	Aluminum sulfate content (g)	0	31	95	160	220	315	380
20	Aluminum oxide layer thickness (nm)	0	50	150	250	350	500	600
	H.V./C	3.8R	4.0R	4.5R	4.1R	4.0R	3.9R	3.1R
25		2.40	2.42	2.72	3.02	3.18	3.06	3.06
		/6.20	/6.44	/6.56	/6.62	/6.46	/6.10	/5.68

As described above, it isn't possible to obtain excellent red color if the iron oxide layer is less than 60 nm.

Also, in case of layer thickness of aluminum oxide being less than 150 nm, the color tone which iron oxide has is emphasized and can not adjust the color tone.

30 As described above, by coating the colorless or white aluminum oxide on the iron oxide coated mica of which color is brown red, it is possible obtain a pigment having the very sharp color and various color tone.

#### EXAMPLE 1

35 100 g of commercially available muscovite is dispersed in 500 ml of water. 10 wt % of ferric chloride (6 hydrate) is added at the 5-ml per minute under heating the system to 90°C and stirring condition. 0.5 N sodium hydroxide solution is added to maintain the pH of the system to 4.5-5.0 until ending of the reaction. The product is filtrated, dried and heated at 500°C for 2 hours. As a result, 136 g of the iron oxide coated mica is obtained.

40 100 g of the iron oxide coated mica, 175g of aluminum sulfate (14 hydrate) and 200 g of urea is dispersed in 1000 ml of water, heated and stirred for 4 hours in the boiling condition. After washing by water, filtering and drying, 127 g of the aluminum oxide coated iron oxide coated mica is obtained by heating at 500°C in the atmosphere.

Obtained powder had vivid appearance color and luster of the purple red.

45 EXAMPLE 2

50 100 g of commercially available iron oxide coated mica (MERCK:IRIODIN 524), 233 g of aluminum sulfate (14 hydrate) and 250 g of urea is dispersed in 1000 ml of water, heated and stirred for 4 hours under the boiling condition After washing by water, filtering and drying, 138 g of the aluminum oxide coated iron oxide coated mica is obtained by heating at 400°C in the atmosphere.

Obtained powder had vivid appearance color and luster of blue red.

#### EXAMPLE 3

55 100 g of commercially available muscovite is dispersed in 500 ml of water. 20 ml of 2M titan sulfate was added under heating the system to 90°C and stirring condition. After washing by water, filtering, and drying, 101 g of the iron oxide coated mica is obtained.

30 g of the titanium oxide coated mica is dispersed in 300 ml of water, 1000 ml of 10 wt % ferric chloride

(6 hydrate) was added at 5 ml / min. At this time, 0.5 N sodium hydroxide solution was added to maintain the pH of the system to 4.5 - 5.0. After filtering and drying, 57.0 g of the iron oxide coated titanium oxide coated mica is obtained by heating at 500°C for 2 hours.

5 50 g of the iron oxide coated mica, 100g of aluminum chloride (6 hydrate) and 100 g of urea is dispersed in 500 ml of water, heated and stirred for 4 hours in the boiling condition. After washing by water, filtering and drying, 61 g of the aluminum oxide coated iron oxide coated titanium oxide coated mica is obtained by heating at 400°C in the atmosphere.

Obtained powder had vivid appearance color and luster of orange.

10 **EXAMPLE 4**

15 100 g of commercially available iron oxide coated mica (MERCK:IRIODIN 524), 260 g of aluminum sulfate (14 hydrate), 20 g of ferric chloride and 300 g of urea is dispersed in 1000 ml of water, heated and stirred for 4 hours under boiling condition. After washing by water, filtering and drying, 146 g of the aluminum oxide coated iron oxide coated mica is obtained by heating at 400°C in the atmosphere.

Obtained powder had vivid appearance color and luster of blue red.

**EXAMPLE 5**

20 50 g of commercially available iron oxide coated mica (MERCK:IRIODIN 524) was dispersed in 500 ml of water. 2000 ml of 10 wt% aluminum sulfate (14 hydrate) solution was added at 10 ml / min. under heating and stirring condition while the pH of the system was maintained 4.5 - 5.0 by adding 1N-sodium hydroxide solution. After washing by water, filtering and drying, 65 g of the aluminum oxide coated iron oxide coated mica is obtained by heating at 400°C in the atmosphere.

25 Obtained powder had vivid appearance color and luster of blue red.

**EXAMPLE 6**

30 100 g of commercially available titanium oxide coated mica (MERCK:IRIODIN 215) was dispersed in 500 ml of water and 2000 ml of 10 wt% ferric chloride (6 hydrate) solution was added in the system at 5 ml / min. under heating at 90 °C and stirring condition. At this time, the pH of the system was maintained 4.5 to 5.0 by adding 0.5N sodium hydroxide solution. After filtering and drying, 160 g of the iron oxide coated titanium oxide coated mica is obtained by heating at 500°C for 2 hours.

35 100 g of the iron oxide coated titanium oxide coated mica, 175 g of aluminum sulfate (14 hydrate) and 200 g of urea is dispersed in 1000 ml of water, heated and stirred for 4 hours under the boiling condition. After washing by water, filtering and drying, 123 g of the aluminum oxide coated iron oxide coated mica is obtained by heating at 500°C in the atmosphere.

Obtained powder had vivid appearance color and luster of orange.

40 **EXAMPLE 7**

45 100 g of commercially available kaolinite, 100 g of ferric chloride (6 hydrate) and 150 g of urea is dispersed in 1000 ml of water, and heating the system at 90°C and stirring for 4 hours under same condition. After filtering and drying, 127 g of the iron oxide coated kaolinite was obtained.

100 g of the iron oxide coated kaolinite, 120 g of aluminum sulfate (14 hydrate) and 250 g of urea is dispersed in 1000 ml of water, heated and stirred for 4 hours under boiling condition. After washing by water, filtering and drying, 116 g of the aluminum oxide coated iron oxide coated kaolinite is obtained by heating at 500°C in the atmosphere.

Obtained powder had vivid appearance color and luster of mandarin-orange.

50 The obtained red pigments according to the example 1 to 7 are examined as described hereinafter.

For comparisons, commercially available coloring titanium oxide coated mica (iron oxide coated mica and carmine added titanium oxide coated mica) were examined as the same method.

The examination is conducted for appearance color tone, acid stability, alkaline stability, light stability, and heat stability.

55 Methods of examination and an examination result are shown below.

① Appearance color tone

5        5 g of the red pigments according to the present invention and commercially available colored titanium oxide coated mica are filled in quartz cells which are for the powder color tone measurement. After sufficient orientation, the powder is pressed at the constant pressure and samples for the measurement is obtained.

The samples are measured the colorimetry by the spectrum colorimetry machine (HITACHI C-2000).

The colorimetry is indicated as the average with three times examination.

② Acid stability

10      1.5 g of the red pigments according to the present invention and commercially available colored titanium oxide coated mica is filled in 50 ml stoppered test tubes. 30 ml of 2-N hydrochloric acid solutions are added to the test tubes. After dispersion, the test tubes are standed on the test tube stand, and observed the color tone after 24 hours.

15      ③ Alkaline stability

20      1.5 g of the red pigments according to the present invention and commercially available colored titanium oxide coated mica is filled in 50 ml stoppered test tubes. 30 ml of 2-N sodium hydroxide solutions are added to the test tubes. After dispersion, the test tubes are standed on the test tube stand, and observed the color tone after 24 hours.

④ Light stability

25      2.5 g of the red pigments according to the present invention and commercially available colored titanium oxide coated mica are filled in inner plates which are made from the 20 mm square aluminum plate at 3 mm thickness and irradiated by a xenon lamp for 30 hours.

30      The color tone of the sample before and after irradiation are measured by the spectrum colorimetry machine (HITACHI C-2000) and obtain color differences ( $\Delta E$ ) before and after irradiation from the colorimetry value.

⑤ Heat stability

35      3.0 g of the red pigments according to the present invention and commercially available colored titanium oxide coated mica are filled in porcelain crucibles and heated at 400 °C for 2 hours in the atmosphere.

The color tone of the sample before and after the heating treatment are measured by the spectrum colorimetry machine (HITACHI C-2000) and obtain color differences ( $\Delta E$ ) before and after the heating treatment from the colorimetry value.

The results of each stability examination were shown in table -8.

40

Table - 7

Pigment to have used for comparison		
Comparison 1	Chroizone rouge franbe	TiO <sub>2</sub> +Mica+Fe <sub>2</sub> O <sub>3</sub>
Comparison 2	Chroizone red	TiO <sub>2</sub> +Mica-Carmine

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Table - 8  
Result of color tone and stability

		Color tone H.V./C.	acid	Stability		
				alkali	light	heat
10	example 1	0.7R 4.0/8.3	◎	◎	0.71	0.81
	2	8.5RP 4.5/8.2	◎	◎	0.74	0.65
	3	7.0R 4.0/9.0	◎	◎	0.82	0.74
	15	9.0RP 4.2/8.2	◎	◎	0.77	0.35
	4	0.5R 4.5/8.0	◎	◎	0.60	0.55
	20	7.5R 4.8/8.1	◎	◎	0.79	0.75
	7	8.0R 3.8/7.1	◎	◎	0.65	0.88
25	Comparison 1	2.8R 4.9/6.9	○	◎	0.77	0.83
	2	2.3RP 5.4/7.5	×	×	22.1	40.3

Evaluation standard :

- ◎ discoloration never admitted and a high stability.
- discoloration is rather admitted but has the good stability
- × Discoloration is admitted and the stability is low.

As is clear from the result in table 2, the red pigment according to the invention can adjust the color tone from the yellow red to the blue red by changing the content ratio of the iron oxide and the aluminum compound by which the plate type particle are coated.

Also, the chroma of the red pigment according to the invention is equal to or higher than that of the chroizone red for the comparison 2 which is added an organic substance.

The inorganic pigment which have the chroma equals to an organic pigment is very rare. Therefore, it is obvious that the color tone of the red plate type pigment according to the present invention is excellent comparing the other inorganic pigment.

As is clear from the table - 8, the stability of the red pigment according to the present invention has the same or excellent stability comparing the commercially available coated iron oxide mica of the comparison 1.

Moreover, the acid stability of the red pigment according to the present invention is excellent rather than the commercially available iron oxide coated mica because the acid solves the iron oxide from the surface of the commercially available iron oxide coated mica. On the other hand, a particle surface of the red pigment according to the present invention is fully coated with the aluminum oxide which is excellent about the acid stability.

Also, the stability of the mica titanium of the comparison 2 which was added carmine is not good under the severe condition, because the stability of the carmine is bad .

As described above, the red pigment according to the present invention has excellent color tone with high chroma from the orange to the blue red and moreover, and excellent stability by coating the surface of plate type iron oxide.

**Claims**

1. A red pigment comprising:

5                   an iron oxide plate type particle,  
                  an aluminum compound layer which contains at least aluminum oxide and which is formed on the  
                  iron oxide particle,  
                  and the optical thickness of the aluminum compound layer being 150-500 nm.

10                 2. A red pigment according to the claim 1, further comprising;

                  an iron oxide layer which is formed on a plate type particle,  
                  the optical thickness of the iron oxide layer being 60-350 nm,  
                  and the optical thickness of the aluminum compound layer being 150-500 nm.

15                 3. A red pigment according to the claim 1, wherein said aluminum compound layer contains 1-20 weight %  
                  of iron oxide and / or compound of iron oxide-alumina.

20                 4. A manufacturing method of a red pigment comprising;

                  forming an iron oxide coated plate type particle of which the content of the coated iron oxide is  
                  from 20 to 100 weight % for the plate type particle by coating a plate type particle using a coating bath  
                  containing a precursor of the iron oxide according to a precipitator method,

25                 forming an aluminum compound coated iron oxide coated plate type particle of which content of  
                  the aluminum compound is from 15 to 60 weight % for the iron oxide coated plate type particle by coating  
                  the iron oxide coated plate type particle using a coating bath containing a precursor of the aluminum com-  
                  pound according to a precipitator method,

                  and heating the aluminum compound coated iron oxide coated plate type particle from 100 to 900  
                  °C.

30                 5. A manufacturing method according to claim 4, characterized in that a precursor of iron oxide is added to  
                  the coating bath of aluminum compound so as to be 1 to 20 weight % of iron oxide and / or iron oxide-  
                  aluminum compound for the iron oxide coated plate type particle.

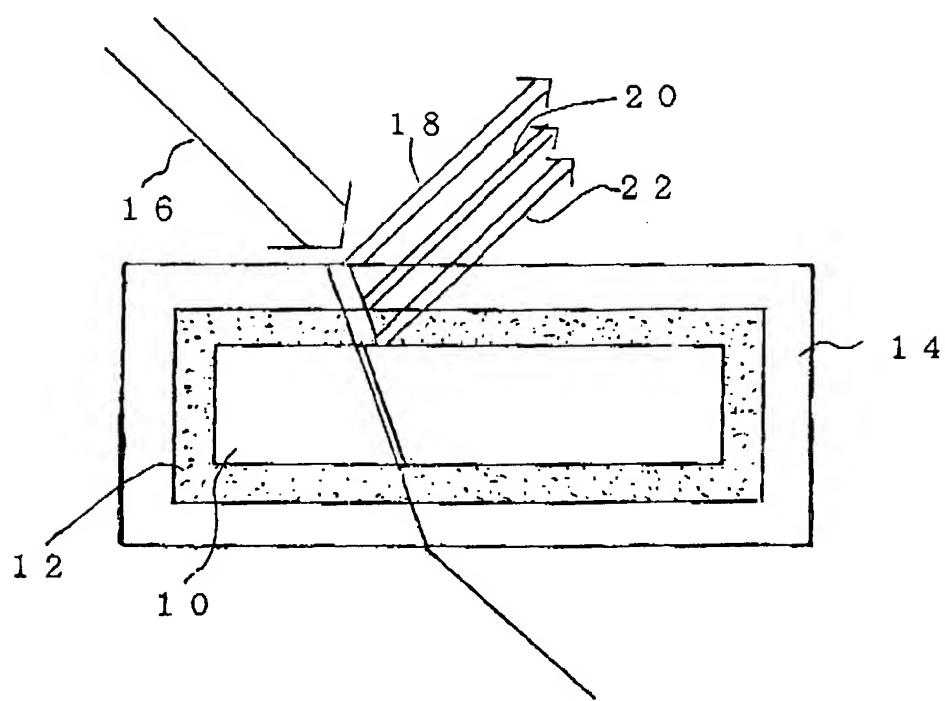
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F I G. 1

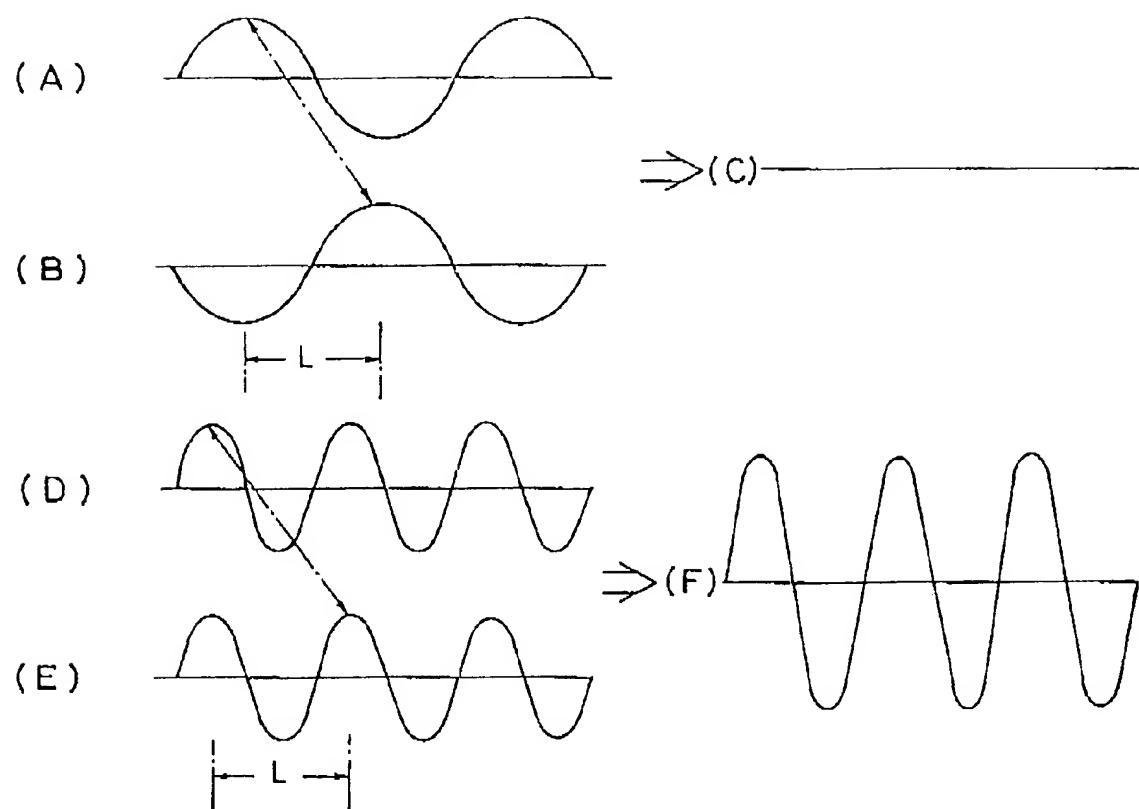


FIG. 2